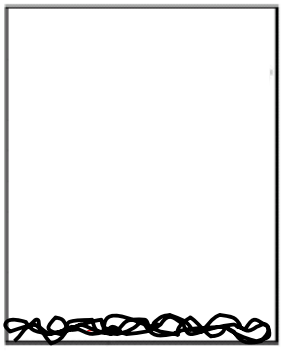
Chapter 5
Formulation - Neutral polymer in solutions

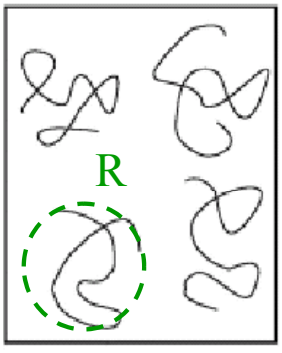
5.1. Conformation of neutral polymers in solution
5.2. Structure and viscosity of dilute suspensions
5.3. Structure and viscosity of semi-dilute suspensions

5.1 Conformation of neutral polymers in solution

Good and bad solvents

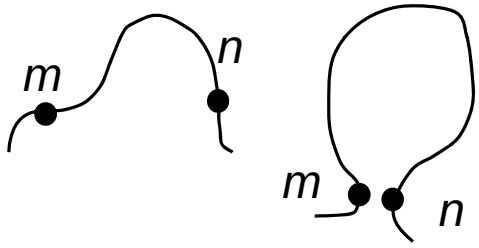


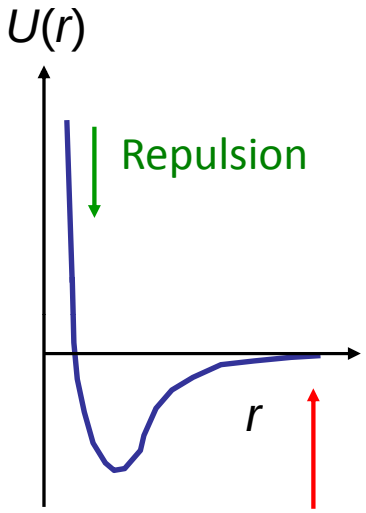
Polymer and solvent are non compatible
Collapse
$R = bN^{1/3}$



Polymer and solvent are compatible
Coil conformation
Radius of the polymer coil?
Interactions between coils?

Definition of the excluded volume





m and *n* cannot be at the same location. A short range repulsion is at the origin of the excluded volume

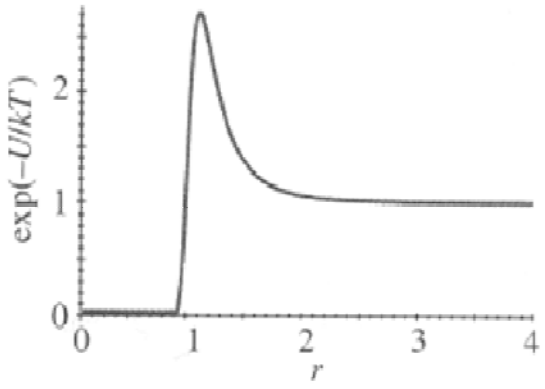
Van der Waals attraction

$U(r)$: interaction potential between two monomers

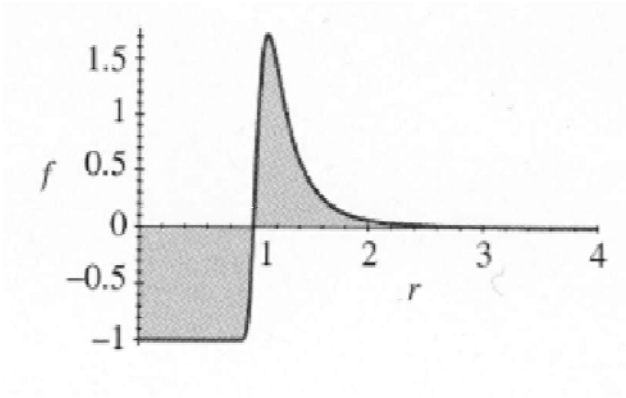
v_e ($\geq b^3$) : excluded volume

Cost of exclusion: kT per monomer

Determination of the excluded volume



Probability that a monomer is at a distance *r* from another monomer:



Probability that a monomer is excluded from a sphere of radius *r* centered on another monomer

$$P(r) \sim \exp\left(-\frac{U(r)}{kT}\right)$$

$$f(r) = 1 - \exp\left(-\frac{U(r)}{kT}\right)$$

Excluded volume: $v_e(T) = \int_0^\infty 4\pi r^2 f(r)\mathrm{d}r = \left(1 - \frac{\Theta}{T}\right) b^3$

Classification of solvents

$$v_e(T) = \int_0^\infty 4\pi r^2 f(r)\mathrm{d}r = \left(1 - \frac{\Theta}{T}\right) b^3$$

T ↑

$v_e = b^3$ in the high temperature limit
hard sphere repulsion/athermal solvent

$v_e > 0$: compatible solvent

$v_e = 0$: solvant Θ (attraction=repulsion):

$R = bN^{1/2}$

$v_e < 0$: bad solvant

non solvent $R = bN^{1/3}$

In the Flory-Huggins description: $v_e = (1-2\chi)b^3$
χ is the polymer/solvent Flory-Huggins parameter

Flory model

Chain of radius R with N monomers of radius b
Number concentration: N/R^3

Probability to have a monomer in volume v_e: $v_e N/R^3$
Free energy associated with the exclusion of one unit: kT

Total free energy of interaction:

$$\frac{F_{\text{int}}}{kT} = \frac{1}{2} N \frac{v_e N}{R^3} = \frac{1}{2} v_e \frac{N^2}{R^3}$$

Configurational entropy ≈ elastic energy

$$\frac{F_{\text{elas}}}{kT} \sim \frac{3}{2} \frac{R^2}{Nb^2}$$

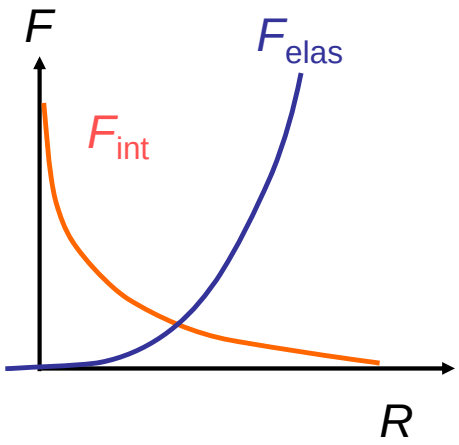
Chain conformation in good solvent

$$\frac{F}{kT} = \frac{3}{2}\frac{R^2}{Nb^2} + \frac{1}{2}v_e\frac{N^2}{R^3}$$

Total free energy

After minimisation: $R = b(v_e/b^3)^{1/5}N^{3/5}$

Advanced theory : $R = b(v_e/b^3)^{0.18}N^{0.588}$



Swelling/ ideal chain ($R = bN^{1/2}$)

Athermal limit ($v_e = b^3$): $R = bN^{\nu}$

For real chains, swelling (ν) depends on the affinity with the solvent.

Characterization of a solution?

c : number of monomers/volume unit

C : concentration in g/cm^3:

$C = cM_0/N_A$

M_0 : molar mass of monomers

N_A : number of Avogadro

ϕ : volume fraction of monomers

$\phi = cb^3$

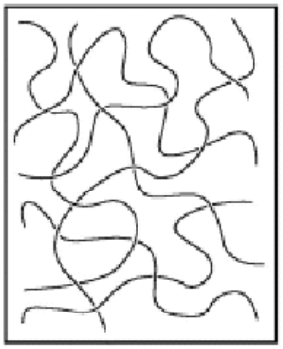
$C = \phi M_0/N_A b^3$

$\phi = N_A b^3 C/M_0$

Structure of polymer solutions

$c < c^*$

$c = c^*$



$c > c^*$

Entanglements

$c > c_e \cong 2c^*$

For athermal solvent: $R = bN^{\nu}$

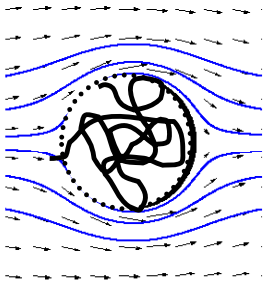
Overlap concentration

$$c^* \cong N/R^3 = \frac{1}{b^3} N^{1-3\nu} \quad \text{or} \quad C^* = \frac{M_0}{N_A b^3} N^{1-3\nu}$$

For large molar masses, C^* is very small

5.2. Viscosity of dilute solutions (c < c*)

Viscosity of dilute suspensions



Zimm viscosity

The flux of solvent does not penetrate the coils (hydrodynamic interactions between monomers). The streamlines around polymer coils are distorted just like for a sphere of radius $R = bN^{\nu}$

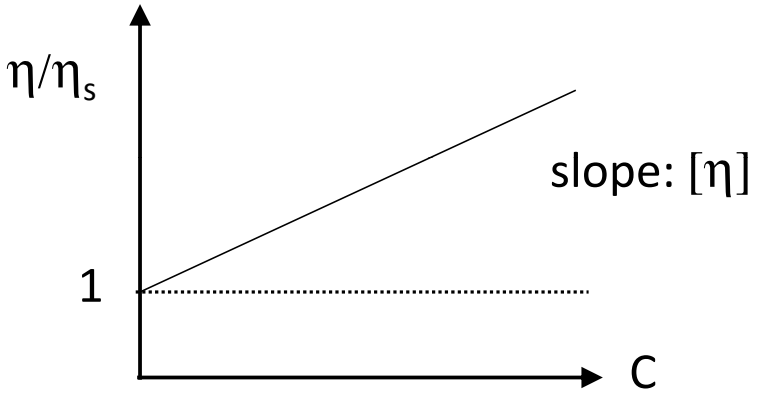
C : monomers concentration (g/cm^3)
N_A : Avogadro number
M : molar mass of the polymer

$$\eta \cong \eta_S \left(1 + \frac{5}{2} \frac{CN_A}{M} R^3 + \ldots \right)$$

La viscosité est égale à $2\eta_s$ pour $C^* \sim 0.4(M/N_A R^3) \sim M^{1-3\nu}$

Definition of the intrinsic viscosity

$$[\eta] == \lim_{C \to 0} \frac{\eta - \eta_s}{C\eta_s}$$



$$[\eta] = \frac{M_0}{N_A b^3} N^{1-3\nu} = \frac{1}{C^*} \propto \frac{R^3}{M} \qquad (cm^3/g)$$

Intrinsic viscosity

$$[\eta] == \lim_{C \to 0} \frac{\eta - \eta_s}{C\eta_s}$$

For hard spheres: $5/2\rho$

Note that the unit is : cm^3/g ! (ex. globular proteins: 4 cm^3/g)

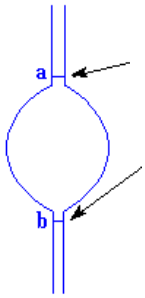
Polymers in Θ solvent: $[\eta] \cong \frac{R^3}{M} \cong M^{1/2}$

Polymers in good solvent: $[\eta] \cong \frac{R^3}{M} \cong M^{4/5}$

In general: Mark-Houwink equation : $[\eta] = KM^a$

(a=2 for rigid rods)

Determination of the intrinsic viscosity



Capillary rheometry:
The container between a and b is filled with solvent and we measure the time it needs to the volume between a and b to flow out of the capillary

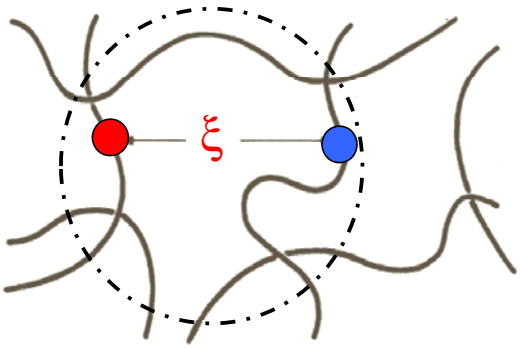
Intrinsic viscosity measurements are useful:

- to determine the solvent quality
- to determine the molar mass
- to measure the Kuhn length (C_∞)
- to determine $c^* \sim 1/[\eta]$

5.3 Structure and dynamics of semi-dilute solutions

Athermal solvent

Correlation length in semi-dilute solutions



ξ: correlation length
Each red monomers is surrounded by solvent and neighbors belonging to the same chain. Beyond ξ they are blue monomers belonging to different chains

Hypothesis:
the properties of the solution (ξ, osmotic pressure, viscoelasticity) only depend on

$$\frac{\varphi}{\varphi^*} \quad or \quad \xi = f\left(\frac{\varphi}{\varphi^*}\right) \approx \left(\frac{\varphi}{\varphi^*}\right)^n$$

$\phi = \phi^*$ $\quad \xi = R$

$\phi > \phi^*$ $\quad \xi$ is independent of N (since it is a function of ϕ/ϕ^*)

Scaling of the correlation length

$$\xi = R\left(\frac{\phi}{\phi^*}\right)^n \sim N^{n(3\nu-1)+\nu}$$

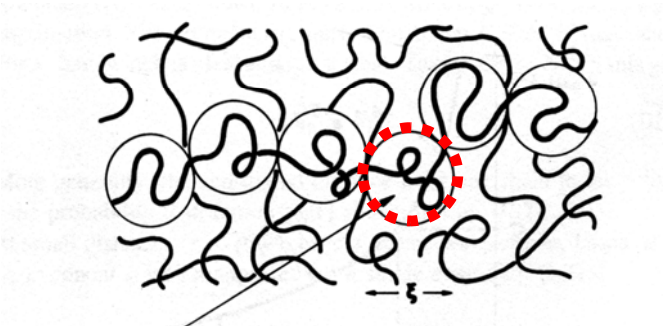
$$\xi \sim N^0 \text{ pour } n = -\nu/(3\nu\text{-}1)$$

$$\xi = b\phi^{-\nu/(3\nu-1)}$$

The correlation length decreases with the concentration!
When $\xi = b$, there are not excluded volume interactions anymore and the chain becomes ideal (the solution behaves like a melt)

For a compatible solvent this limit is reached for $\phi^{**}<1$
A concentrated solution behaves like a polymer melt

Correlation volume



$$\phi = \frac{gb^3}{\xi^3}$$

The volume of correlation or «blob» has a diameter ξ and comprise g monomers. Inside a blob there are excluded volume interactions
A blob behaves like an inpenetrable sphere

$$\xi = bg^{\nu}$$

$$\xi = b\phi^{-\nu/(3\nu-1)}$$

$$g = \phi^{-1/(3\nu-1)}$$

Structure at large distance

At distances> ξ, excluded volume interactions are screened and the chain is ideal

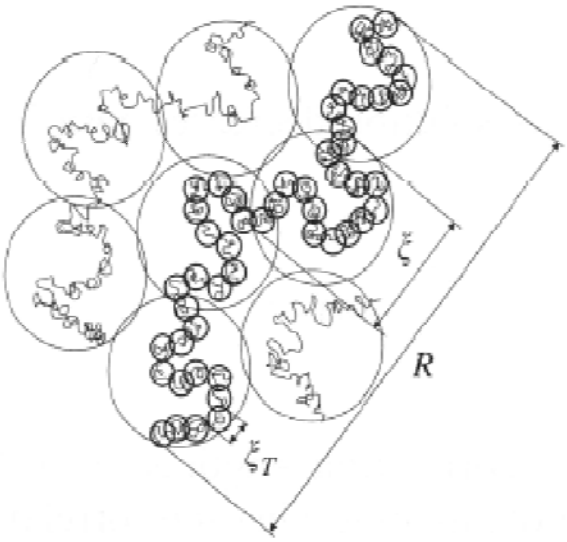
$$R \approx \xi \left(\frac{N}{g} \right)^{1/2}$$

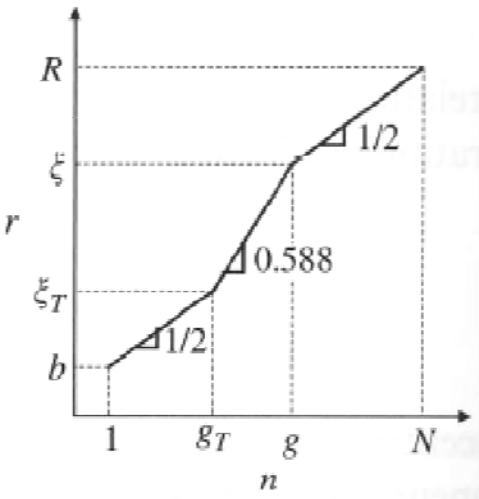
Blob (semi-dilute solution) ⟶ Monomer (melt)

$$R \approx \xi \left(\frac{N}{g} \right)^{1/2} \approx bN^{1/2}\phi^{-(2\nu-1)/(6\nu-2)}$$

With ν=3/5: $\xi = b\phi^{-3/4}$ et $R = bN^{1/2}\phi^{-1/8}$

Summary





For athermal solvent: $\xi_T = b$

Multiscale structure of a chain in good solvent (ν = 3/5)

Non-entangled semi-dilute regime

Hydrodynamic interactions are screened beyond ξ
Therefore each chain can be seen as a chain made of *N/g* blobs with diameter ξ

Each blob follows a Zimm dynamics because it is non penetrable to the solvent. Its relaxation time is

$$\tau_\xi \cong \frac{\eta_S \xi^3}{kT}$$

In the absence of entanglements chains move according to the Rouse model:

$$\tau_R \propto \tau_\xi \left(\frac{N}{g}\right)^2 \propto \frac{\eta_S}{kT}\xi^3 \left(\frac{N}{g}\right)^2$$

Scaling laws in the non-entangled regime (ν=3/5)

$$\xi \propto b\phi^{-3/4}$$

$$R \propto bN^{1/2}\phi^{-1/8}$$

$$\tau_R \propto \frac{\eta_S}{kT}\xi^3 \left(\frac{N}{g}\right)^2 \propto \tau_0 N^2 \phi^{1/4}$$

$$\tau_0 \propto \frac{\eta_S b^3}{kT}$$

$$D \propto \frac{R^2}{\tau_R} \propto \frac{kT}{\eta_S b} N^{-1}\phi^{-1/2}$$

$$G_0 \propto \frac{\phi RT}{N}$$

$$\eta_0 \propto \eta_S N \phi^{5/4}$$

Dynamics of entangled chains

1 - Hydrodynamic interactions are screened beyond ξ

2 – The tube diameter is proportional to (but larger than) ξ

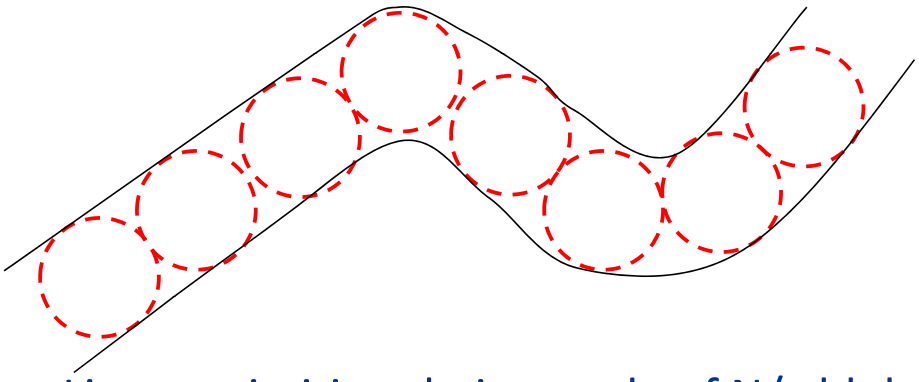
$$d(\phi) = d_0 \phi^{-\nu/(3\nu-1)}$$

$$R \approx \xi \left(\frac{N}{g}\right)^{1/2} \approx b N^{1/2} \phi^{-(2\nu-1)/(6\nu-2)}$$

Separability of length scales

Dilute regime	Semi-dilute non-entangled	Semi-dilute entangled
Zimm dynamics	Rouse dynamics	Reptation
Hydrodynamic interactions	Hydrodynamic interactions < ξ	Hydrodynamic interactions < ξ Entanglements

Reptation in entangled solutions



$d \sim \xi$
$L \sim (N/g)\xi$
$\nu = 3/5$

Linear primitive chains made of N/g blobs

Curvilinear diffusion of the chain along the tube

Friction on a blob: $6\pi\eta_S\xi$

Friction on the chain inside the tube: $6\pi\eta_S(N/g)\xi$

Curvilinear diffusion coefficient: $$D_l = \frac{kT}{6\pi\eta_S(N/g)\xi}$$

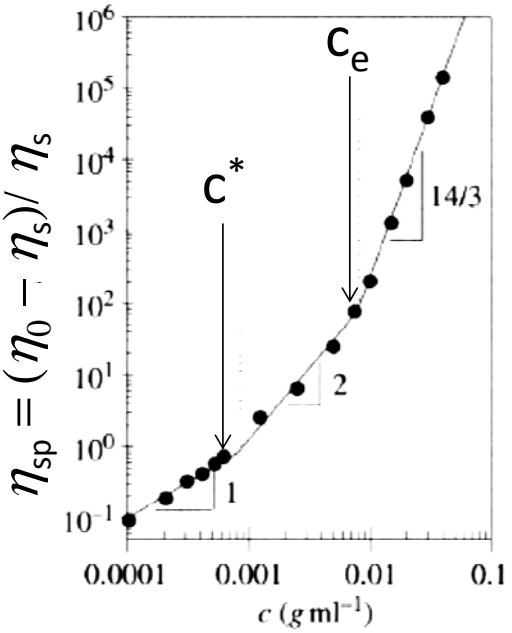
Longest relaxation time $$\tau_d = \tau_0 N^3 \phi^{3/2}$$

Elasticity and viscosity of entangled solutions

Plateau modulus: $$G_0 = \frac{kT}{\xi^3} = \frac{kT}{b^3}\phi^{9/4}$$

Low-shear viscosity: $$\eta_0 = \eta_S N^3 \phi^{15/4}$$

Example



Exponent 2 :
Rouse model with $\nu = ½$
(θ solvent)

Specific viscosity of poly(ehtylene oxide): $M_W = 5\times10^6$ g/mol

M. Rubinstein et R Colby, Polymer Physics